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ABSTRACT

CONTINUOUS MONITORING OF VOLATILE ORGANIC COMPOUNDS IN AIR EMISSION USING MEMBRANE EXTRACTION MICROTRAP GC SYSTEM

by
Xin Zhang

A novel method for continuous monitoring volatile organic compounds (VOCs) in air at trace level is presented. A membrane module and a microtrap were used along with gas chromatographic analysis. The membrane module consisted of a bundle of silicone rubber hollow fibers and separated the VOCs from the gaseous stream. The microtrap which is a very small adsorbent trap played the roles of preconcentrator and injector. The VOCs selectively permeate across the membrane into a strip gas in the membrane module. Before entering the GC column, the VOCs are trapped and concentrated by the microtrap. Desorption of the VOCs is accomplished by direct electric heating. A concentration pulse is generated by fast heating, which act as an injection for GC separation. Continuous monitoring is done by making injections at fixed intervals of time, while the emission stream flows continuously through the membrane module. In this study, the performance of the system was evaluated and the different parameters were studied.

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VOLATILE ORGANIC COMPOUNDS IN AIR EMISSION USING
MEMBRANE EXTRACTION MICROTRAP GC SYSTEM**

by
Xin Zhang

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Submitted to the Faculty of
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in Partial Fulfillment of the Requirement for the Degree of
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APPROVAL PAGE

CONTINUOUS MONITORING OF
VOLATILE ORGANIC COMPOUNDS IN AIR EMISSION USING
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This thesis is dedicated to
Kun-ling Tang, my dear mother

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CHAPTER 1

INTRODUCTION

1.1 Air Analysis

Environmental protection has become a major concern in recent years. Volatile Organic Compounds (VOCs) are a group of pollutants that even at very low concentrations may be hazardous to public health. Many of the VOCs such as aromatic and halogenated organics are toxic, mutagenic, and/or carcinogenic. VOCs also lead to ozone formation in the troposphere. They are usually present in very low concentrations (ppbv to ppmv level). The detection and quantitative measurement of these contaminants at trace levels in air emissions is of considerable importance. The development of rapid and sensitive analytical techniques is necessary to monitor these pollutants present in the environment and to keep track of what is being emitted from different sources.

Traditional monitoring efforts in the industrial environment involves collection of a sample from a process or waste stream, and then transporting it to a central laboratory for analysis. Usually, analysis is done hours, or days after a sample is collected. EPA approved methods to analyze for VOCs in ambient air and stack emissions use either whole air samplers such as Tedlar bags and canisters (EPA Method TO14) or sorbent cartridges (EPA Method TO1) [1]. In the whole air sampling devices, a few liters of the sample are collected and then brought back to the lab for analysis. In the sorbent based method, the sample is passed through a cartridge containing one or more adsorbents, where the VOCs are trapped. The VOCs are recovered by thermal desorption or solvent extraction for analysis. While these methods are quite effective in VOCs' detection and measurement, there are some disadvantages. The major limitation is that there is a

long delay between sampling and analysis. Moreover, the analysis cost for these methods is quite high and this limits the number of samples that can be analyzed.

In view of environmental monitoring, the analytical results are critical and should be reported as soon as possible. Callis et al [2] discussed the need for on-line analysis in process analytical chemistry. On-line analyzers are designed to eliminate the delay between sampling and analysis. Basically, on-line analysis involves two critical steps: (1) the measurement of process parameters and (2) the conversion of the measurement data to process information. This information is then used to document, correct, and improve process performance. In general, on-line analysis provides information on a continuous basis about what is going on in the process, or what kind of pollutants are being released. Some of the advantages of on-line analysis are: reduces sampling error, eliminates problems associated with handling and transport of sample, reduces the time lag between sampling and analysis, provides continuous analysis, and facilitates process control. On-line techniques provide a more accurate analysis of VOCs by reducing errors such as loss of VOCs and sample contamination.

Although micro-sensor technology has provided some possibilities for real-time monitoring, specific sensors are not available to identify and quantitate the wide range of compounds. Infrared methods and mass spectrometry has been used in real-time monitoring of stack gas [3, 4] but there are serious limitation, such as interference from CO₂, CO and H₂O which are always present in stack emissions..

Chromatographic separation is good for analysis of complex VOCs mixtures because of its separation capabilities. Recently, automated GC systems have been designed for air analysis on a semi-continuous basis. However, in all these devices the sample flows through a sorbent tube for a period of time and then the sorbent tube is thermally desorbed to release the analyte for GC analysis [5, 6]. Usually, a cycle time of several hours is encountered. The instrumentation is not

available at present that can be used to continuously separate and identify trace level VOCs components in air emission.

The objective of this research is to develop an analytical system for continuous monitoring of VOCs in air emissions. Most emission streams are a complex mixture and along with VOCs many contain H₂O vapor, CO₂, SO₂ and NO_x etc. Some of these background gases may interfere with VOCs analysis. In the system developed here, the VOCs are allowed to selectively permeate through a membrane into an inert gas. The VOCs are then concentrated and injected into a GC for analysis. The membrane permeation occurs in a membrane module containing several hollow fiber silicone membranes. The concentration/injection of VOCs is done using a microtrap.

In air monitoring, the concentration of VOCs to be analyzed is usually quite low, from ppb to ppm levels. Thus it is necessary to accumulate the sample from a large volume of air, prior to GC analysis. Direct injection of large samples into GC is not possible because this causes excessive band broadening and degrades chromatographic resolution. On the other hand, a very small injection volume reduces sensitivity. To do real-time GC monitoring of VOCs at trace level, it is necessary not only have an automatic injection device but also a sample preconcentrator. In this research, an on-line microtrap is used for the dual purpose of sample preconcentration and injection, and a membrane module is used for separation of VOCs from gas stream and enrichment of sample concentration.

1.2 On-line Microtrap

The important feature of any continuous, on-line GC instrumentation is the sample introduction device, which is required to make automatic, reproducible injections. To do real-time GC monitoring of trace concentrations, it is necessary to have an automatic injection device that also acts as a sample preconcentrator. Recently,

the development of an on-line microtrap for continuous monitoring of VOCs in air emission has been reported [7, 8].

An on-line microtrap is made by packing a small diameter tubing with an adsorbent. The sample containing the analyte is introduced into the analytical column through the microtrap. The analytes are trapped by the adsorbent as the stream passes through the microtrap and can be thermally desorbed by rapid electrical heating. When the heating is rapid enough, the "desorption pulse" can serve as an injection for the GC column. Corresponding to each injection, a chromatogram is obtained. Due to its small size and thermal mass, the microtrap can be heated and cooled rapidly, and injections can be made every few seconds. The electric pulse is controlled by an electronic timer which can turn on and off the power automatically. The pulse duration and the interval between pulses can be easily controlled. The capacity factor of the microtrap is changed at different temperature. Consequently, the concentration of the sample is changed. Thus, the on-line microtrap can be used as a substitute for automatic valves that are commonly used in process GCs. A very low detection limit is reached when using the on-line microtrap because of its function as a preconcentrator.

1.3 Membrane Extraction of VOCs

The use of membranes to separate gaseous mixtures is one of the most exciting and significant emerging technology in recent years. Membrane separation processes are often more capital and energy efficient when compared with conventional separation processes [9]. Introduced commercially only in late 1979, this technology has found worldwide acceptance in a range of industrial, medical, and laboratory applications. Typical applications include air separation (O_2/N_2) and dehumidification, hydrogen recovery from a variety of refinery and petrochemical streams, removal of impurities from natural gas, recovery of carbon

dioxide from enhanced oil recovery operations, and recovery of helium from dirigible and diving atmospheres [10].

There are many examples of technology involving diffusion of a gas or vapor through a microporous-type membrane [11-14]. Acetoacetate is decarboxylated to acetone, which is separated from the sample by gas diffusion through a microporous membrane of Teflon resin and measured spectrophotometrically. Similar methods have been developed for ammonia and other gases such as CO_2 and SO_2 [15]. Van der Linden developed an expression for the membrane transport process and tested it for gas-diffusion transport of several volatile compounds across microporous hydrophobic membranes. The transport is directly related to the volatility of the compound. Cortes and Davis [16] used a bundle of dialysis hollow fibers to separate monomers and low-molecular-weight components from a latex solution and sequentially quantify the permeate by liquid chromatography.

There are two types of membrane that can be used for gas separation. The first is a "porous" membrane in which the gases are separated on the basis of their molecular size by diffusion through small pores. The world's first and largest gas separation membrane plant was based on inorganic porous membranes [17]. The vast majority of commercial applications are based on "nonporous" gas membranes. These contain no holes or pores in the conventional sense. They rely on the principle that gases dissolve in and diffuse through solid materials. The mechanism of nonporous permeation membranes is a combination of solubility and molecular diffusion. The transmission of permeate through a polymer membrane is an activated diffusion process. The permeate first dissolves in the permeable membrane on the side of its higher concentration. Then it diffuses through the membrane towards the side of the lower concentration, a process which depends on the formation of holes in the plastic network due to thermal

agitation of the chain segments. Finally, the permeate desorbs on the side of the lower concentration.

One of the first analytical application of nonporous membrane was described by Westover et al. [18]. In this application, a silicone rubber membrane was used as an interface between water samples and a mass spectrometer. The volatile compounds which permeated through the membrane probe were drawn into the ion source for analysis. Melcher [19] used a silicone rubber membrane in membrane-assisted liquid chromatography. In this application, compounds permeating the membrane were concentrated in an extractant and automatically injected into a liquid chromatographic system. That work demonstrated the ability of membranes to separate and concentrate organic compounds, even of low volatility, from sample matrices which could not be directly injected into a chromatographic system. The use of a membrane to pretreat a sample that cannot be directly injected is a significant improvement in the art of chromatography.

Membrane gas separation uses asymmetric semi-permeable polymeric material for separating different constituents of a feed gaseous stream. The vast majority of gas separation membranes are based on polymers and constructed as either flat sheets or hollow fibers. Flat sheet membranes are manufactured in long rolls and then assembled into plate-and-frame or spiral-wound configurations. The spiral-wound approach provides a higher area/volume ratio than the plate-and-frame system and is thus the most common configuration for flat sheet systems. Hollow fibers are small tubes that have outer diameters ranging from as little as 50 microns to over 500 microns. Hollow fibers provide even higher packing densities than spirals. Hollow fiber gas permeators are somewhat more common than the spiral wrap type mainly because of their higher surface area to volume ratio. Table 1 shows the surface area to volume ratio of different types of membrane module [20]. The degree of separation achievable in a membrane permeator

depends on the feed and permeate flow patterns. The idealized flow pattern is counter current [21].

Table 1 Approximate Membrane Surface Area Per Unit Volume of Module

Module Type	Area /Volume (ft. ² /ft. ³)
Tubular	100
Spiral Wound	300
Hollow fiber	5000

1.4 Theory of Membrane Extraction

The permeation of a gas through a nonporous polymeric membrane is a complex process that may involve the following sequence of steps: (a) adsorption of the permeate at the membrane interface, (b) solution of the gas into the membrane at that interface, (c) activated diffusion of the permeate through the membrane, (d) release of the gas from solution at the opposite interface, and finally, (e) desorption from the latter interface. Steps *a* and *b*, as well as *d* and *e*, are not necessarily distinct. The term *permeation* is therefore used to describe the overall mass transport of gas across the membrane, whereas the term *diffusion* refers only to the movement of the gas inside the membrane matrix [22].

1.4.1 General Considerations

Barrer [23] and other investigators [24, 25] showed that activated diffusion is usually the rate-controlling step in the permeation process. Diffusion of a gas in a membrane can be described by Fick's first law, which takes the following form for one-dimensional transport in a direction normal to the membrane interfaces:

$$J = -D (\partial C / \partial X) \quad (1)$$

where J is the rate of diffusion of the penetrant gas through a unit reference area; D is the diffusion coefficient for a specific penetrant-membrane system and temperature; and C is the concentration of the penetrant in the membrane at a position coordinate X .

According to Equation (1), the flux J is proportional to both the diffusion coefficient and the concentration gradient, $\partial C / \partial X$, measured normal to the reference area. The diffusion coefficient for systems of gases and polymeric membranes can be constant or a function of penetrant concentration. It can also depend on position coordinate, and on time. The concentration gradient can be obtained from Fick's second law:

$$\partial C / \partial t = \partial (D \partial C / \partial X) / \partial X \quad (2)$$

where $\partial C / \partial t$ is the rate of change in concentration with time, t , at a position coordinate X . Solutions of this partial differential equation have been summarized by Barrer [23], Crank [26], and Jost [27] for constant as well as variable diffusion coefficients, for a variety of geometries and boundary conditions, and for both steady-state and transient flow. Experimental methods for the determination of diffusion coefficients have been reviewed by the above authors and by others.

The concentration of a gaseous penetrant in a polymeric membrane is dependent on the solubility of the penetrant in the polymer. Under conditions of solution equilibrium, the relation between the pressure p of the penetrant in the gas phase and its (uniform) concentration C in the polymer is usually expressed in the form:

$$C = S(c) p \quad (3)$$

or

$$C = S(p) p \quad (4)$$

where $S(c)$ and $S(p)$ are solubility coefficients reported as functions of concentration or pressure. When the penetrant solubility is sufficiently low, Equations (3) and (4) reduce to Henry's law:

$$C = S_0 p \quad (5)$$

where the solubility coefficient S_0 is a constant for any specific penetrant-membrane system and temperature.

1.4.2 Effect of Pressure

Equation (1) can be integrated across the thickness of the membrane, δ , to yield

$$J = D_0 (C_h - C_l) / \delta \quad (6)$$

Where C_h and C_l are the penetrant concentrations at the membrane interfaces; the subscripts h and l signify "high" and "low" ($C_h > C_l$). It is more practical to express the rate of permeation in terms of the penetrant gas pressures P_h and P_l on the two sides of the membrane, in equilibrium with C_h and C_l , respectively. Thus substitution of Equation (5) in Equation (6) results in the expression

$$J = (D_0 S_0) (P_h - P_l) / \delta \quad (7)$$

Finally, the total rate of gas permeation, G , through a planar membrane of area A is derived for steady-state conditions from Equation (7):

$$G = JA = P_0 (A \Delta P / \delta) \quad (8)$$

where

$$P_0 \equiv D_0 S_0 \quad (9)$$

P_0 is usually called the "permeability coefficient," the "permeability constant," or simply the "permeability," and ΔP ($= P_h - P_l$) is the difference between the pressures on the two sides of the membrane. The permeability coefficient depends only on the nature of penetrant-membrane system and the temperature. Consequently, the rate of permeation through a planar membrane is directly

proportional to the permeability coefficient, the membrane area, and the pressure differential, and is inversely proportional to the membrane thickness.

Permeation through a tubular membrane can be expressed corresponding to Equation (8)

$$G = P_0 2\pi h(P_h - P_l) / \ln(r_o/r_i) \quad (10)$$

where h is the length of the tube. The inner and outer radii of the tube are r_i and r_o , respectively.

1.4.3 Effect of Temperature

Both the diffusion and the solubility coefficients for penetrant-membrane systems are usually exponential functions of temperature and can be expressed by the following Arrhenius-type relations: [24, 28]

$$D = D_0 \exp(-E_d/RT) \quad (11)$$

and

$$S = S_0 \exp(-\Delta H_s/RT) \quad (12)$$

where E_d is the energy of activation for diffusion, ΔH_s is the enthalpy of solution, R is the universal gas constant, T is the absolute temperature, and D_0 and S_0 are constants. By virtue of Equation (9), the permeability coefficient is also an exponential function of temperature.

$$P = P_0 \exp(-E_p/RT) \quad (13)$$

where E_p is the energy of activation of the permeation process and P_0 is a constant. From Equations (9), (11), (12), and (13), it is seen that

$$E_p = E_d + \Delta H_s \quad (14)$$

The sign of E_p in Equation (14) depends on the following factors. The solution of a gas in a polymer can be visualized as a two-step process involving (a) condensation of the gas, which occurs exothermally, followed by (b) mixing of the condensate with the polymer, which is an endothermic step.

Hence, ΔH_s can be considered as the sum of two terms:

$$\Delta H_s = \Delta H_{cond} + \Delta H_1$$

where ΔH_{cond} is the enthalpy of condensation of the penetrant gas, and ΔH_1 is the partial molar enthalpy of mixing. For simple gases above their critical temperature, ΔH_{cond} is a hypothetical quantity and its value is relatively small; hence ΔH_s will be approximately equal to ΔH_1 and positive. Since E_d is always a positive quantity, E_p will also be positive and, according to Equation (13), the permeability coefficient for penetrant-membrane systems will increase exponentially when the temperature is raised. For example, the methyl bromide-polyethylene system is illustrated in Figure 1, showing the dependence of permeability coefficient on temperature and pressure. The Arrhenius plot for P at a constant pressure at 100 torr is linear. The isobars at higher pressures pass through a marked minimum as the temperature is lowered, which is explained by the opposite temperature dependence of D and S, as shown in Figure 2.

CHAPTER 2

RESEARCH OBJECTIVE

The object of this research is to develop an analytical system for continuous monitoring of VOCs in air emissions. It will be able to separate and identify the different VOCs at trace levels which are commonly encountered in air samples. In this research a microtrap is used as a continuous injection device, and a membrane module is used for separate the VOCs from whole air sample. The various parameters affecting the response of this system will be investigated.

CHAPTER 3

EXPERIMENTAL

3.1 Instrument

The experimental system used in this research is shown by schematic diagram in Figure 3. The membrane module was constructed from a piece of tubing with hollow fiber membranes going through it. It consists of the membrane module, the microtrap and a GC with an FID or a PID detector.

The membrane module is a tubing cell including 20 pieces of hollow fiber membrane. (Figure 4) The membrane used throughout the study was Dow Corning Silastic medical-grade tubing. The membrane material is a poly (dimethylsiloxane) elastomer. It is chemically, physically and thermally stable. The size of the membrane used was 0.012-inch-i.d. \times 0.025-inch-o.d. (Dow Corning Corporation, Midland, Michigan). At both ends of the tubing cell, the membrane fibers were fixed and attached to the inside wall of the tubing with Epoxy and silica glue. The Epoxy is a high strength sealant which was able to seal both ends of the membrane module and endure high pressure as well. The active length of the fiber was about 20 cm. The air sample was flowed inside the hollow fibers, and the stripping gas flowed countercurrent on the outside of the membrane fibers.

The microtrap was made by packing a 0.53mm i.d. deactivated fused-silica lined stainless steel tubing with 60 mesh Carbotrap C (Supelco Inc., Supelco Park, PA, USA) The length of the microtrap was about 14 cm. The electrical resistance of the microtrap was about 1.2 Ω . The thin walled, small diameter stainless steel tube has low thermal mass allowing rapid heating and cooling. The current through the microtrap was between 5 and 10 A and was controlled by putting additional power resistors in the circuit. Power resistors were put in series with the microtrap

to control the current through it. More details can be found about the resistive heating process [7, 29]. The current through the microtrap was supplied by a Variac (STACO Energy Products CO.) It was controlled by an electric intervalometer (GraLab Model 451 Digital Timer, DIMCO-GRAY COMPANY). With this timer, the electric current supplied to the microtrap for heating could be turned on for a prespecified duration and at a fixed interval of time. Current pulses were applied every 30 seconds to 3 minutes and the duration of each pulse was approximately 1.2 second. Since the microtrap operation is so fast, it is difficult to measure the exact heating rate and the final temperature accurately by using conventional temperature measuring devices. A measurement using a thermocouple showed that temperature as high as 300°C was reached in 1 to 2 seconds.

A Varian GC (Model 3400) equipped with a conventional flame ionization detector (FID) or a photoionization detector (PID) was used in this study. A 30 m long, 0.315 mm i.d. widebore, DB-624 column (J&W Scientific, Folsom, CA, USA) with a 1.8 μ m film of stationary phase was used for separation. The injection port of the GC was bypassed and the sample was introduced directly into the column through the microtrap. Typical flowrates for FID were: air 300 ml/min, Hydrogen 30 ml/min and Nitrogen make up gas 20 ml/min. The detector temperature was 250°C. The carrier gas was nitrogen. The data acquisition was done by an integrator (Dionex, 4290).

3.2 Reagents

All the chemicals used in this experiment were chromatographic grade. The standard gas was made by Liquid Air Cororation (Alphagaz, Morrisville, PA, USA). The gas supply of the whole experiment system and GC was zero grade (Spectra Gases Inc., Newark, NJ, USA).

3.3 Sampling

The standard gas from Alphagaz was used as the sample to demonstrate the working status of the experiment system. Different concentrations of sample were also made in the lab by the use of canister and a small gas cylinder.

The method used to prepare VOCs sample in canister and small gas cylinder was basically according to the method published by J.P. Hsu et al [30]. The canister or the cylinder was cleaned by evacuating and filling with zero grade nitrogen. This was repeated several times. The VOC solutions were injected into the canister or the cylinder through a septum. The canister or cylinder was then charged with zero grade nitrogen to a pressure of 40-psi.

Occasionally, diffusion tubes were used to generate a VOCs containing stream. Liquid samples were placed in the bottom of diffusion capillary tubes which were then inserted into the sample holder. The samples evaporated from the capillary tubes into a flow of air. The evaporation rate was adjusted by varying the capillary diameter, length of the capillary tubes, the height of the liquid level in the capillary tubes and was determined by using the method given by Savitzky and Siggia [31].

3.4 Analysis

The air sample flowed through the membrane module, inside the membrane fibers. Nitrogen (stripping gas) flowed countercurrent around the membrane fibers and carried the permeated VOCs from the membrane module to the GC column. Before entering the GC column, the VOCs were trapped by the microtrap. The microtrap was heated (or pulsed) at regular intervals. A chromatogram was obtained for each pulse. Intervals between pulses could be anything from a few seconds to several minutes. In a typical operation, the microtrap was heated with a 5-10 amp current for a duration of 0.5 to 1.5 second. All transfer lines were heated

to 100°C to prevent any condensation of VOCs. The operating conditions of the gas chromatograph are shown in Table 2.

Table 2 Operating Conditions of Gas Chromatography

Injector	Temperature	90°C
Column	DB-624 (J&W Scientific)	
	Temperature	100°C
	Carrier Gas (N ₂)	5 ml/min
Detector	Flame Ionization Detector (FID)	
	Temperature	250°C
	Attenuation	1
	Range	10
	Air	300 ml/min, 40 psi
	H ₂	30 ml/min, 40 psi
	Make up gas (N ₂)	20 ml/min, 40 psi

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Performance of Monitoring Device

The operation of the analytical system is demonstrated by continuously monitoring a standard gas mixture whose composition simulated the emission from a hazardous waste incineration (Figure 5). It contained 1 ppm each of benzene, toluene, ethylbenzene, trichloroethylene along with combustion products such as CO₂, CO, SO₂ etc. The standard gas flowed continuously through the membrane module at the flow rate of 15 ml/min. The microtrap was pulsed every 3 minutes. The parameters of temperature programming in GC operating conditions are listed in Table 3. A chromatogram of the four compounds was obtained each time an injection was made. Good precision in peak height, peak shape as well as retention time was obtained showing that the membrane extraction process along with microtrap injections were quite reproducible. The heating-cooling cycle of the microtrap is very short, so that it can be pulsed every few seconds. However, the time required for GC analysis may not be that short. Thus, the interval time between pulses is mainly determined by the time required for GC separation. It will be advantageous to reduce the separation time as much as possible.

The performance of this analytical system was also demonstrated in Figure 6 where the sample stream contained xylene, toluene, and chlorobenzene and analysis was done using a photoionization detector (PID). The chromatogram also showed good separation and reproducibility.

Table 3 Parameters of Column Temperature Programming for Continuous Monitoring of Standard Gas

Initial Column Temperature	85°C
Hold Time	0.9 min.
Final Column Temperature	150°C
Column Rate Increase	50°C/min.

4.2 Quantitative Aspects of the Analytical System

The calibration curves of several VOCs for this membrane extraction microtrap GC system are presented in Figure 7. A linear relationship between system response and VOCs concentration was observed in the low to high ppm range. Samples used here were trichloroethylene (TCE), ethyl benzene and toluene. Detection limits for each of these compounds are presented in Table 4. Low detection limits were seen by using this analytical system.

The detection limit is calculated as:

$$\text{Detection Limit} = 3 D_{\text{blank}} / m \quad (15)$$

where, D_{blank} is the standard deviation of blank, m is slope of calibration curve. The most generally accepted qualitative definition of detection limit is that it is the minimum concentration or weight of analyte that can be detected at a known confidence level [32]. This limit depends upon the ratio of the magnitude of the analytical signal to the noise, which is the statistical fluctuations of the blank. That is, unless the analytical signal is larger than the blank by some multiple k of the variations in the blank due to random errors, certain detection of the analytical signal is not possible. As the limit of detection is approached, the analytical signal approaches the mean blank signal S_{bl} . The minimum distinguishable analytical

signal S_m is then taken as the sum of the mean blank signal S_{bl} plus a multiple k of the standard deviation of the blank.

$$S_m = S_{bl} + k D_{blank} \quad (16)$$

Experimentally, S_m can be determined by performing 20 to 30 blank measurements, preferably over an extended period of time. The resulting data are then treated statistically to obtain S_{bl} and D_{blank} . According to the definition of the detection limit C_m :

$$C_m = (S_m - S_{bl})/m \quad (17)$$

Equation (16) is substituted into Equation (17), resulting expression is given as:

$$C_m = k D_{blank} / m \quad (18)$$

As recommended by Kaiser [33], a reasonable value for the constant is $k = 3$. He points out that it is wrong to assume a strictly normal distribution of results from blank measurements and that when $k = 3$, the confidence level of detection will be 89% or greater in all cases. In a recent discussion of detection limits, Long and Winefordner [34] also recommend the use of $k = 3$. As a result, the detection limit is calculated by the Equation (15).

Table 4 Detection Limits for Selected VOC Components

Compound	Slope of Calibration Curve (m)	Detection Limit (C_m)
Toluene	1607.95	5.66ppb
Ethyl benzene	842.64	10.8ppb
Trichloroethylene	500.72	18.2ppb

4.3 Optimization of Analytical System

4.3.1 The Effect of Pulse Interval

The system response and detection limit depend upon the preconcentration effect of the microtrap. By increasing the pulse interval, more analyte is accumulated in the microtrap and consequently the detector response is increased and detection limit lowered. The response of the system for different compounds to different pulse intervals is shown in Figure 8. Toluene, trichloroethylene (TCE) and acetone were used in this experiment. It is seen that the response increased with pulse interval up to a point beyond which the response stayed constant. Beyond the maximum interval, the sample begins to breakthrough and the response cannot be increased further by increasing the pulse interval. In the rising part of curve, the response is directly proportional to the pulse interval. The maximum time for which the microtrap can accumulate sample is the time required for the sample to migrate through the microtrap. Different compounds have different maximum times because the capacity factor for different compounds in carbotrap is different.

4.3.2 Effect of the Sample Air Flow Rate

The effects of sample flow rate on the detector responses for four compounds are shown in Figure 9. The compounds used here were acetone, trichloroethylene (TCE), toluene and ethylbenzene. As flow rate increased, the response of the system increased and reached a maximum point. Beyond that point the response did not increase with the flow rate.

The resistance to mass transfer can be separated into three parts. The first part is diffusion to the membrane, the second is the permeation/diffusion through the membrane and the third is the diffusion in the inert gas phase outside. Diffusion coefficient in the gas phase are two to three order of magnitude higher than that through the membrane. So the mass transfer through the membrane is the

rate limiting step. It has been shown that as flow rate is increased, the extraction efficiency decreases. When flow rate is increased, more analytes molecules came in contact with the membrane. So eventually it reaches a point that even if flow rate is increased there no net increase in analyte throughput across the membrane. At high flow rates analyte diffusion in the membrane determines the rate of extraction. As a result, response does not increase with flow rate.

The flow rate also effects gas permeation because as it is increased, there is more mixing at the sample/membrane interface. Consequently, the formation of the boundary layer was reduced. When the flow rate is high enough, the boundary layer reaches a minimum or is eliminated. Thus further increasing the flow rate does not increase sample throughput anymore.

4.3.3 Effect of Temperature of Membrane Module

The effect of the temperature of the membrane module on the system response is shown in Figure 10. It is seen that at first the responses increased with the increase of temperature. Beyond a temperature of about 70°C, the responses decreased with increase in temperature. This phenomenon showed the decrease in permeability for VOCs due to their reduced partitioning into the membrane at higher temperatures. Permeation of analytes through membrane is a product of diffusivity and solubility coefficient. Diffusion of the molecules in the membrane is an activated process. The diffusion coefficient is temperature-dependent and obeys the Arrhenius equation:

$$D = D_0 \exp(-E_d/RT) \quad (11)$$

Increasing the temperature of the membrane increases the detector response because of the increase of the VOCs diffusion coefficient. On the other hand, the solubility of VOCs in silicone rubber membrane decreases with increase in temperature:

$$S = S_0 \exp(-\Delta H_s/RT) \quad (12)$$

At higher temperature, the decrease in solubility dominates and consequently the response of the system decreases.

4.3.4 Effect of Moisture in Sample Air

The analysis was also performed with an air sample containing quantities of moisture. The results are presented in Figure 11. It is shown that as we go from a dry sample to low moisture content sample, the response of the system decreased. Once beyond a moisture content of about 1%, the response of the system did not change significantly. Silicon rubber is highly water-repellent and retains high surface resistivity under moisture-condensing conditions. Water absorption for this material is almost one percent [35]. Permeation is a function of the properties of both the permeant and the membrane polymer substrate[36, 37]. Similar behavior has been seen for diffusion of water vapors through methyl cellulose membrane [38]. It was found that diffusion coefficient decreased up to moisture content of 3% beyond which it stayed constant. It was hypothesised that as water content increased, it form a mono-layer of moisture which form a resistance barrier to mass transfer. Now the VOCs molecules not only have to pass through the membrane, but also through this moisture layer. Above a certain moisture level the interaction between the moisture and the membrane stays constant and no effect in sample throughput is seen.

4.3.5 Response Time of the Analytic System

The response time of the system was studied using different compounds. The results are shown in Figure 12. Dichloromethane (DCM), methanol and toluene were used as samples. It is shown that there is a delay between sample injection and detector response. It was defined as lag time in diffusion by Frisch [39].

Time lag is the interval from the moment the gas comes into contact with the membrane until it emerges at a constant rate on the other side. Calculation of lag time can be quite complicated because the diffusion process depends upon several different factors. When diffusion coefficient of the gas is a constant, the lag time, L , can be calculated using a simple expression:

$$L = l^2 / 6 D_0 \quad (19)$$

where D_0 is the diffusion coefficient of the gas, and l is the thickness of the membrane [39, 40]. For a certain compound D_0 depends upon the type of membrane, the temperature, cross-linking and chemical nature of the polymer, the structure and polarity of the diffusing molecule. It may also depend upon the concentration of the diffusing species [41]. In general smaller molecules tend to diffuse faster than larger molecules. It has been shown that permeability increases with the critical point of the molecule. Among the three compounds used in this experiment, DCM has the most polarity, and the molecular size of toluene is larger than the other two compounds. As a result, the diffusion rate of DCM was the fastest and that of toluene was the slowest among the three. Consequently, the lag time of the compounds were in the order toluene > methanol > DCM.

The response time also has contribution from dead volume of the system. As a result, a larger membrane module shows a longer delay time although lag time remains constant. Response time can be decreased by using thinner membrane, designing a membrane module with lower dead volume.

CHAPTER 5

CONCLUSION

The thermal desorption microtrap was proved to function as a sample preconcentrator as well as an automatic injection device for GC in our laboratory's previous work [8]. In this research, a silicon rubber membrane module was put into the system and was shown to be effective to act as a gas separator. VOCs in the sample air permeate through the membrane, are trapped and injected by microtrap into the GC for analysis. The performance of this system was demonstrated. It is shown that the on-line membrane extraction microtrap GC system can be used to provide continuous, real time monitoring of VOCs in air emission. A low detection limit (at ppb level) was obtained by using this analytic system.

In this research, several parameters of this system were investigated. It is seen that the system can be used at a temperature not exceeding 70°C. The flow rate of sample air suitable for this system is above 20ml/min. Moisture in sample air has little effect at high content. At this point, the membrane module serves as a moisture remover.

APPENDIX A

Thermodynamic Properties for Methyl Bromide

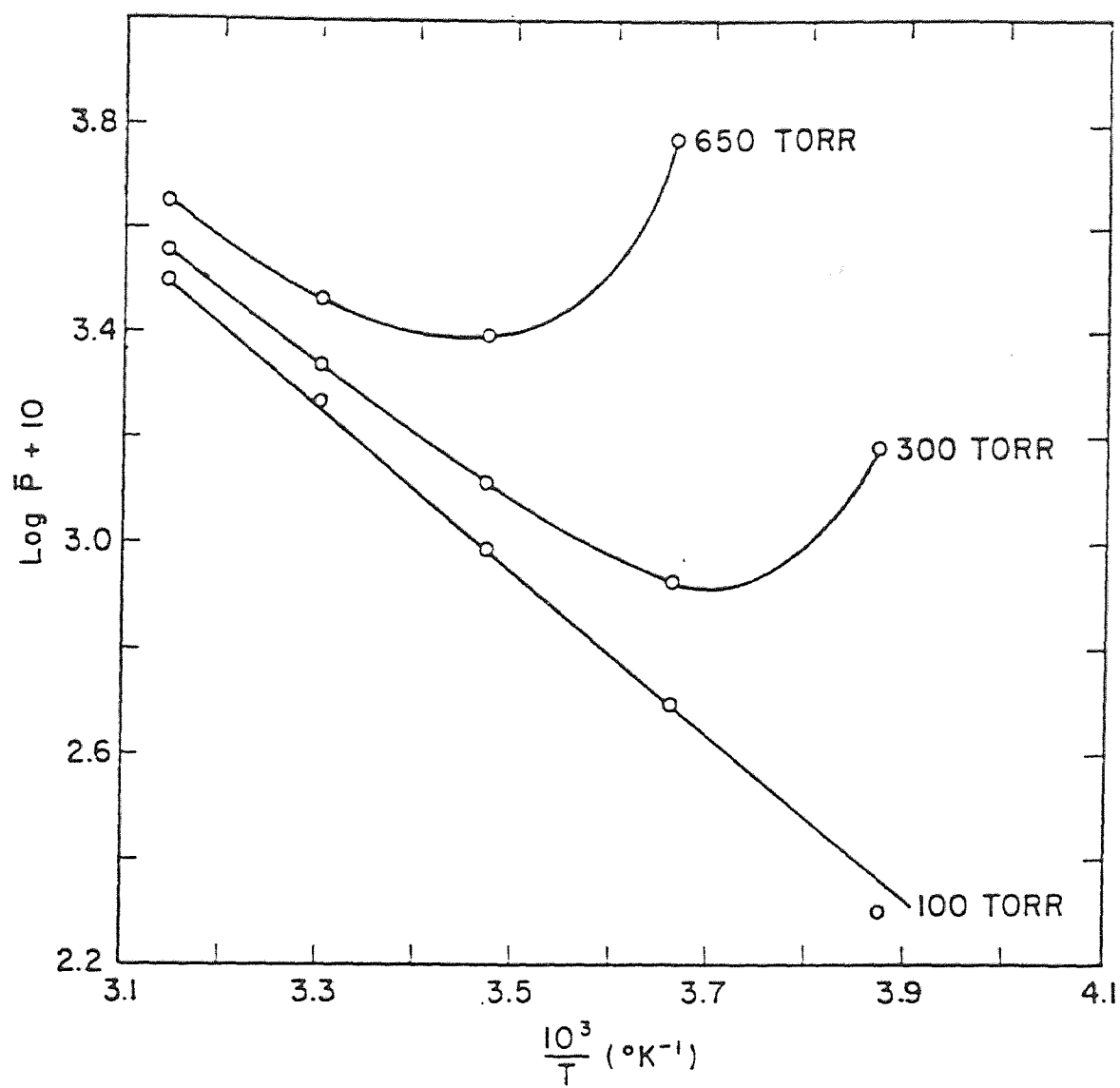


Figure 1 Permeability Coefficients for Methyl Bromide in Polyethylene —
Dependence of Permeability Coefficient on Temperature and Pressure

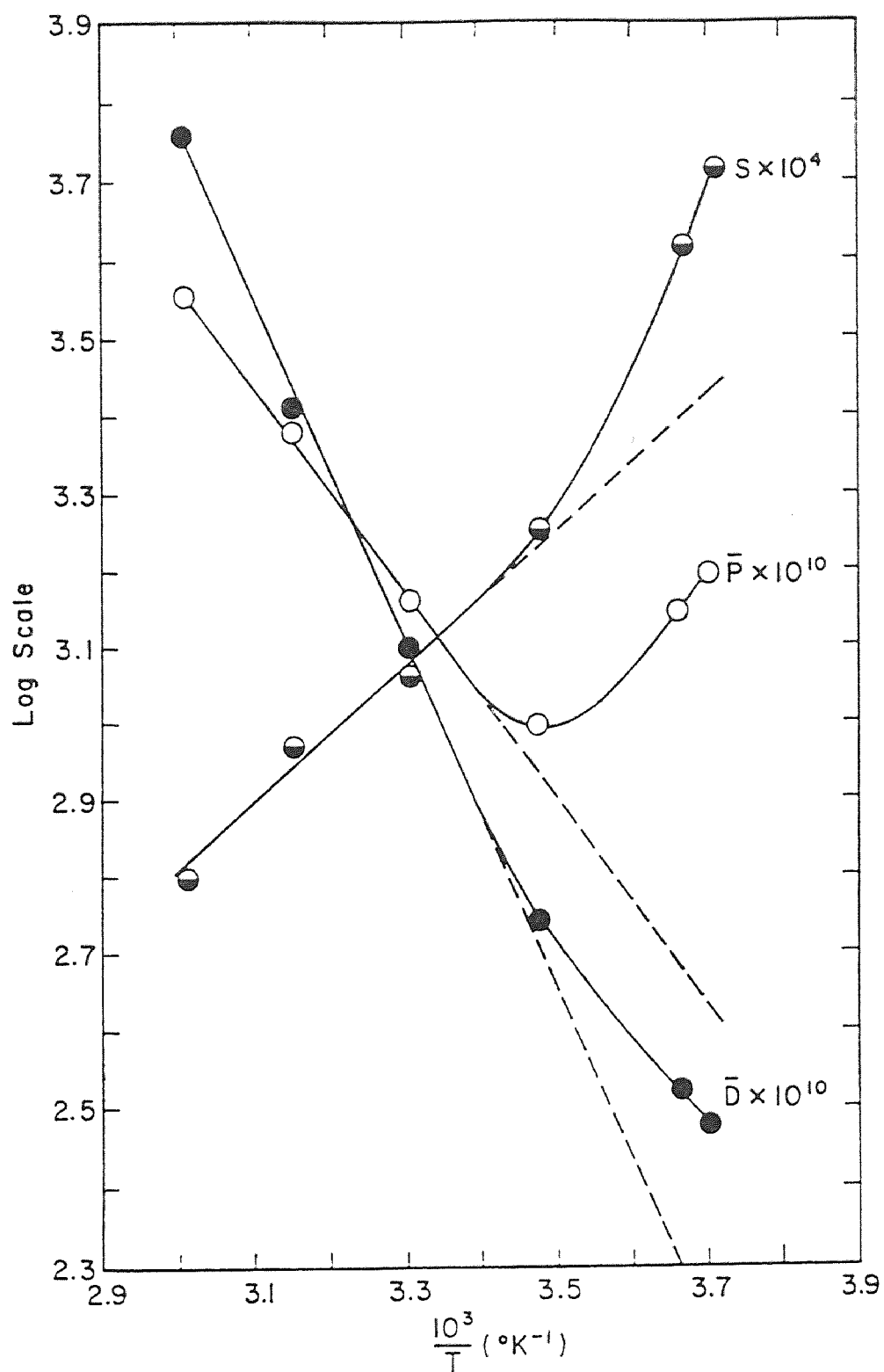


Figure 2 Permeability, Diffusion, and Solubility Coefficients for Methyl Bromide in Polyethylene at 650 torr

APPENDIX B

Experimental Apparatus

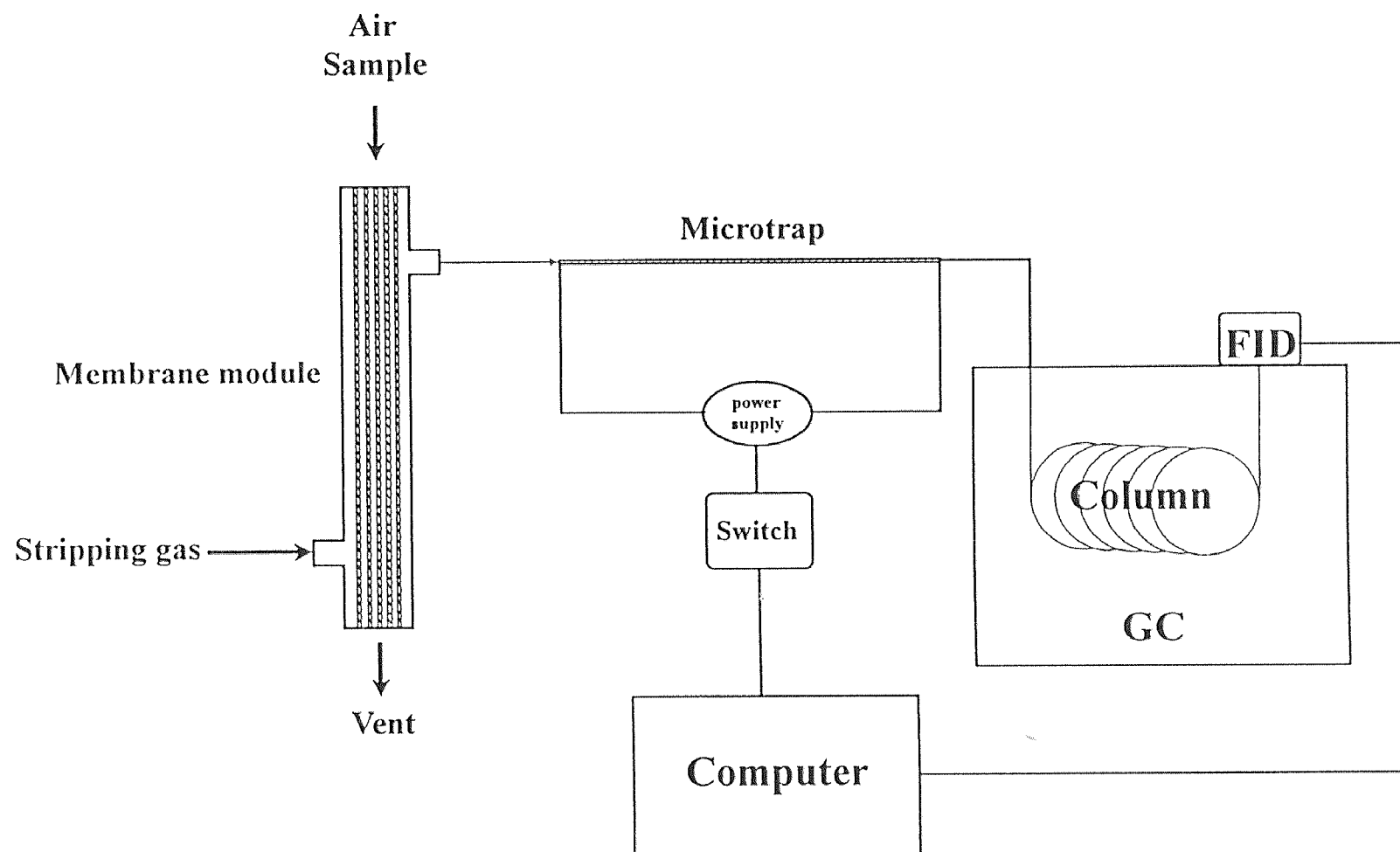


Figure 3 On-line Membrane Extraction Microtrap GC System

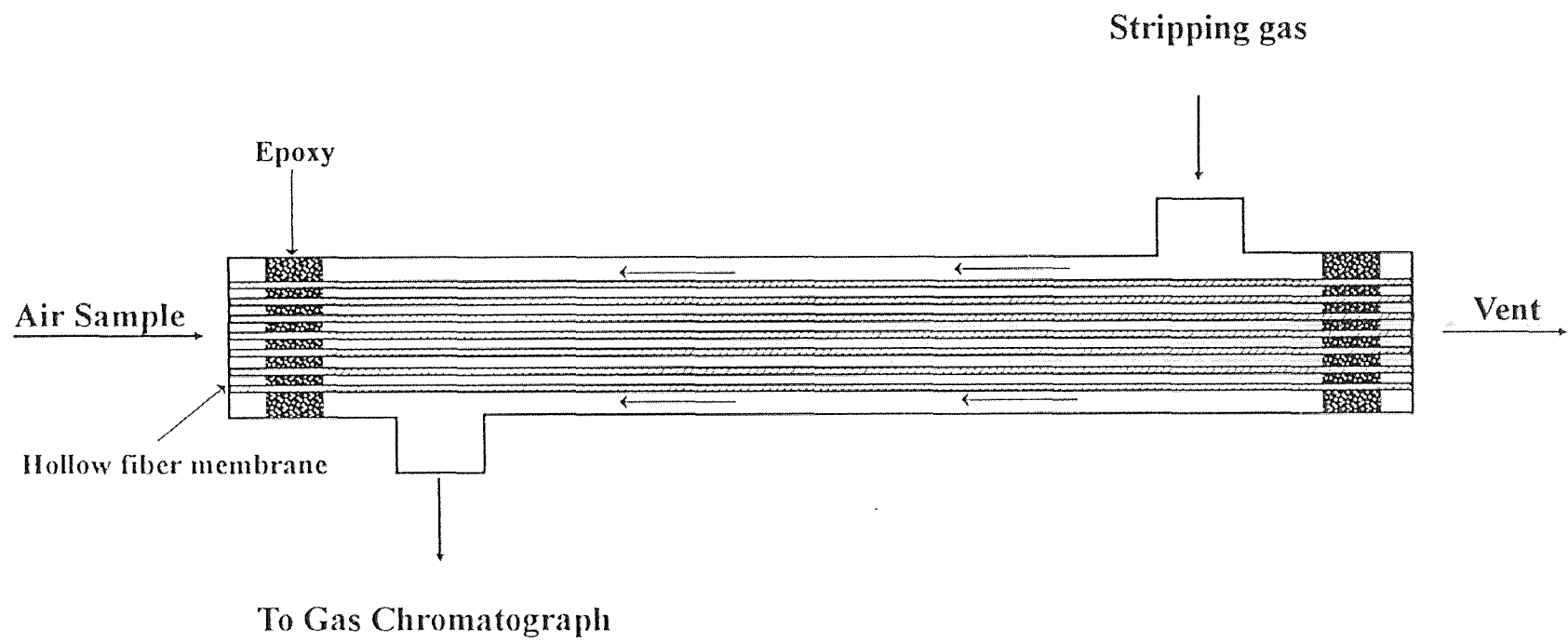


Figure 4 Membrane Extraction Module

APPENDIX C

Experimental Observations

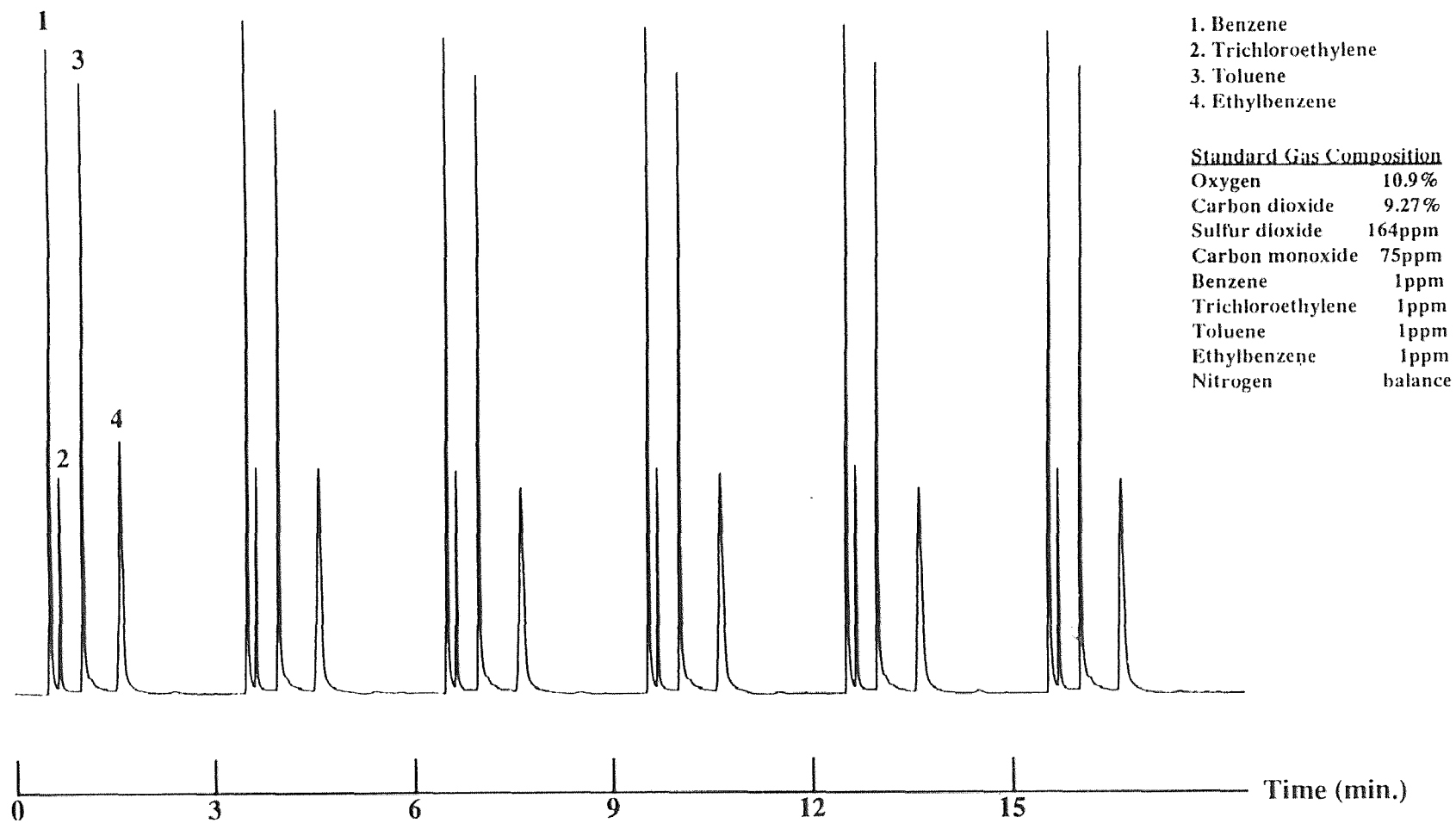


Figure 5 Continuous Monitoring of Simulated Stack Gas

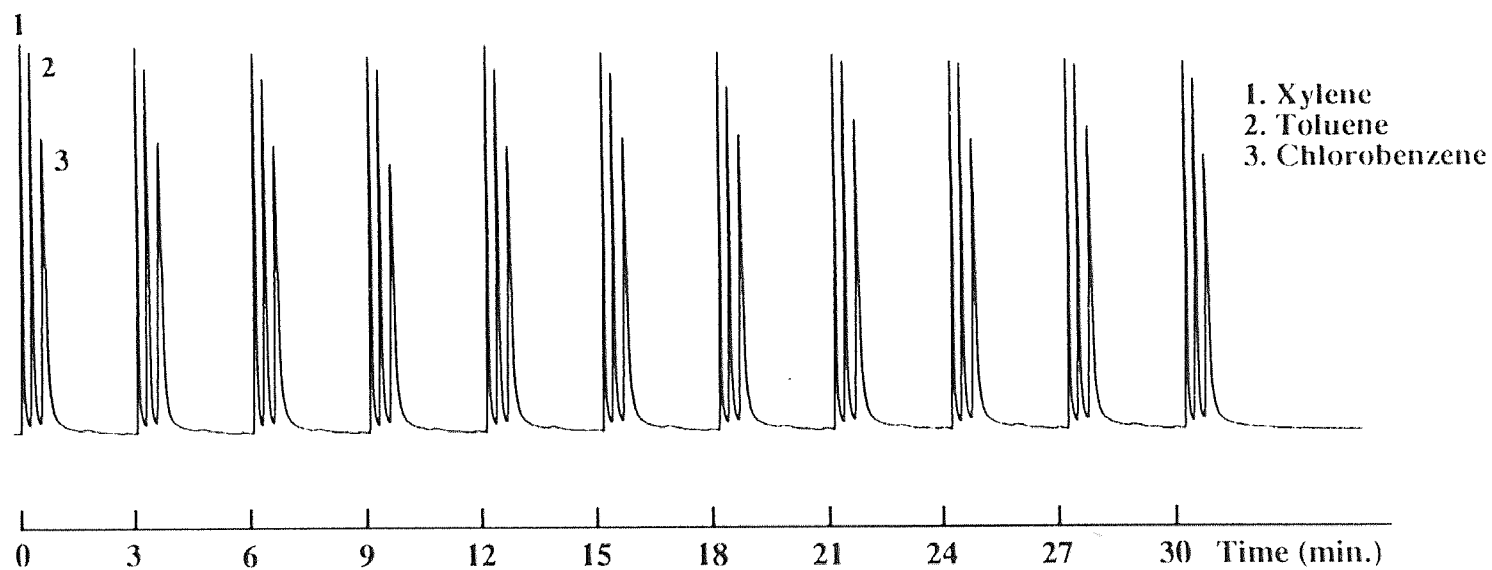


Figure 6 Continuous Monitoring of Aromatic VOCs Using Photoionization Detector

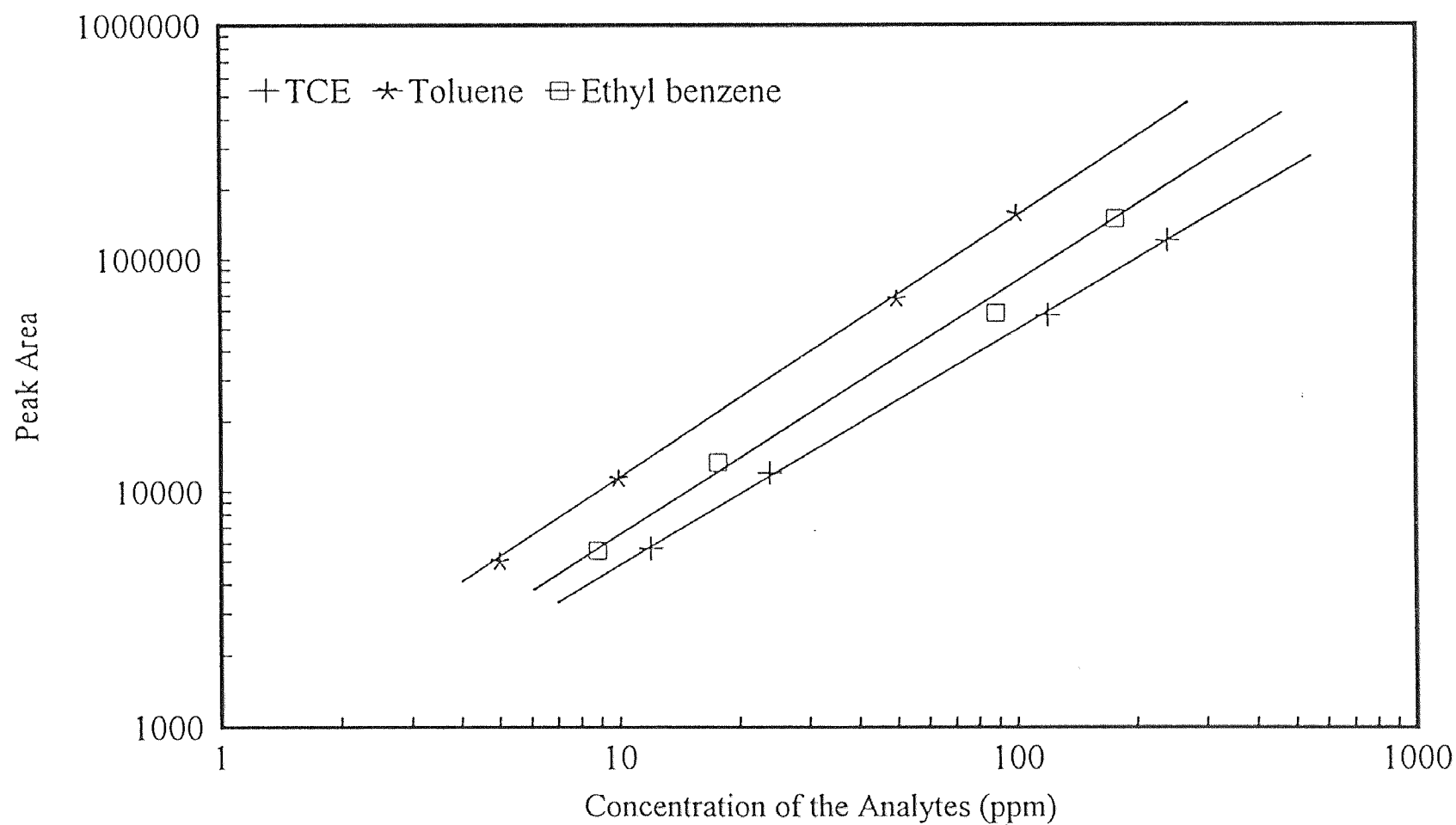


Figure 7 Calibration Curve for Different VOCs

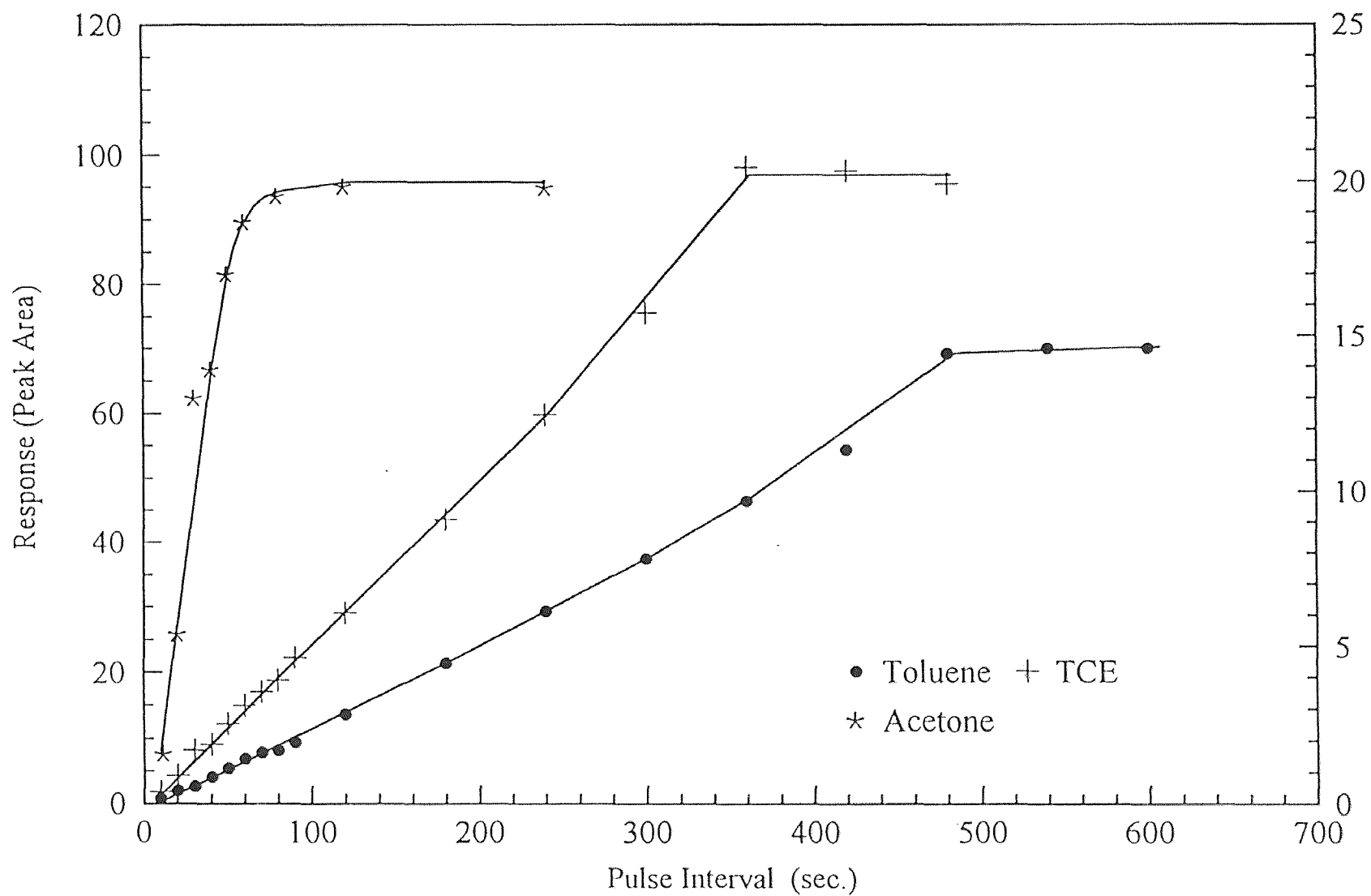


Figure 8 Response of the System at Different Pulse Interval

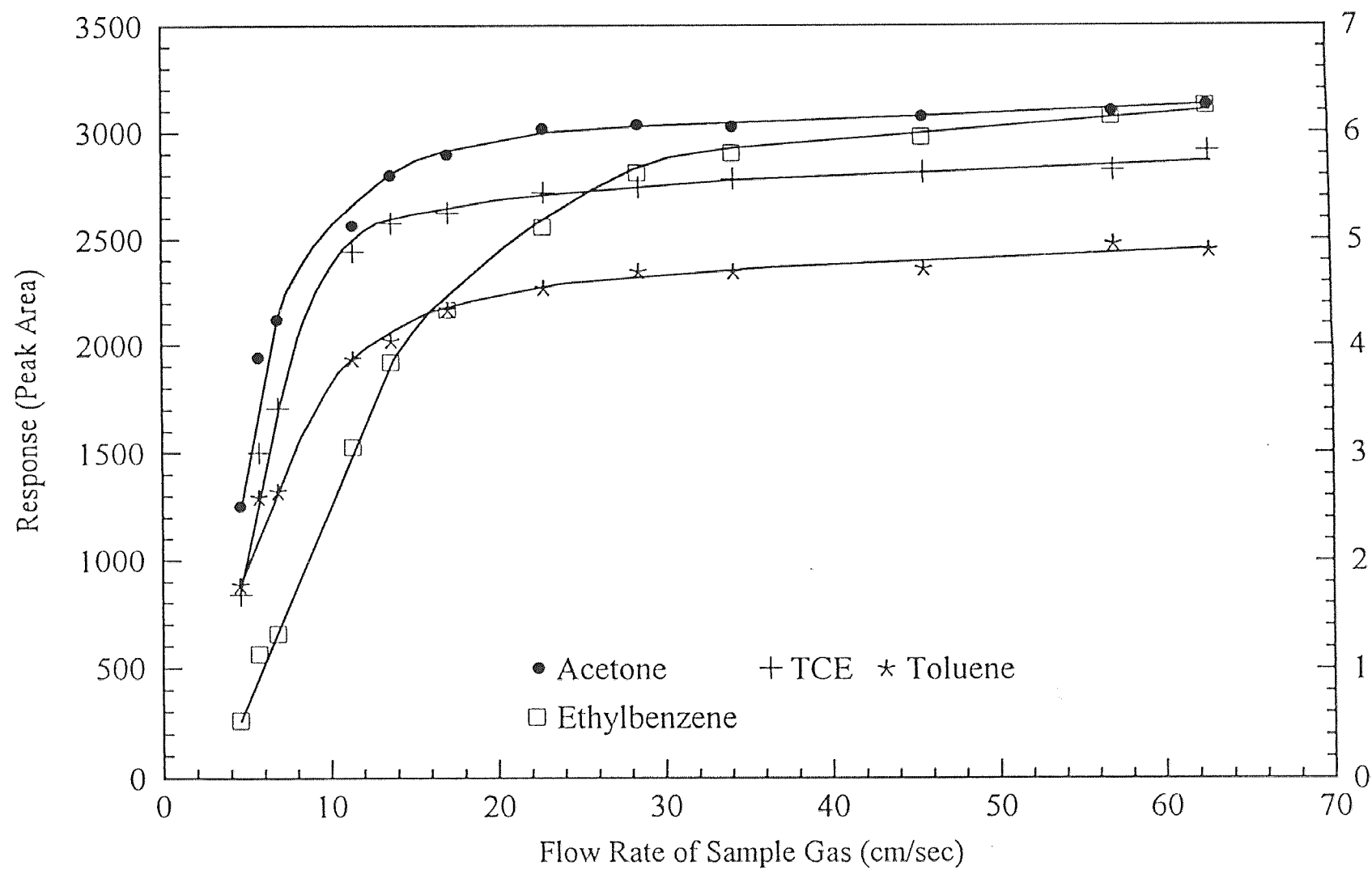


Figure 9 Effect of the Flow Rate of Sample Gas on Response

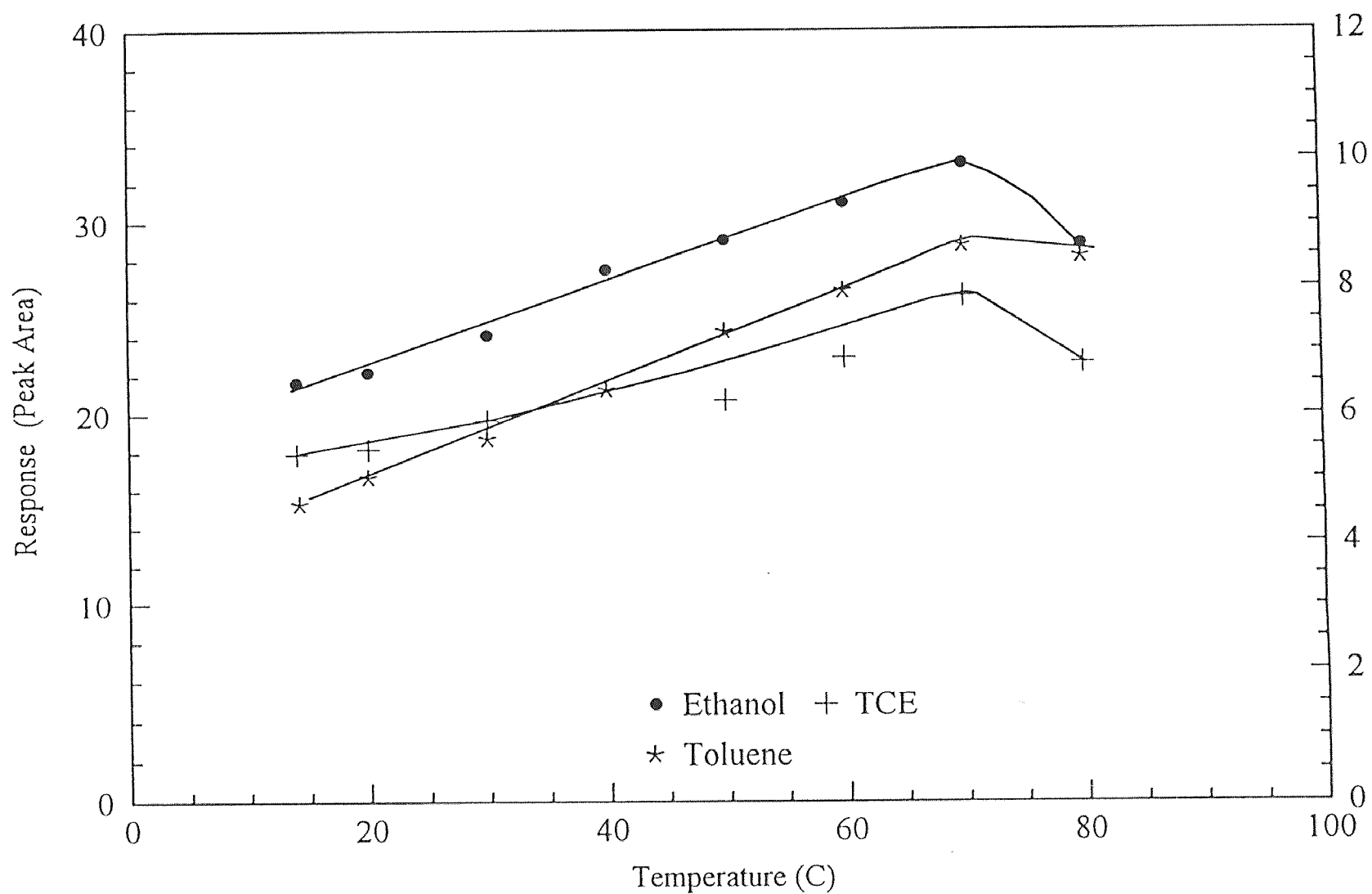


Figure 10 Effect of Membrane Temperature on Response

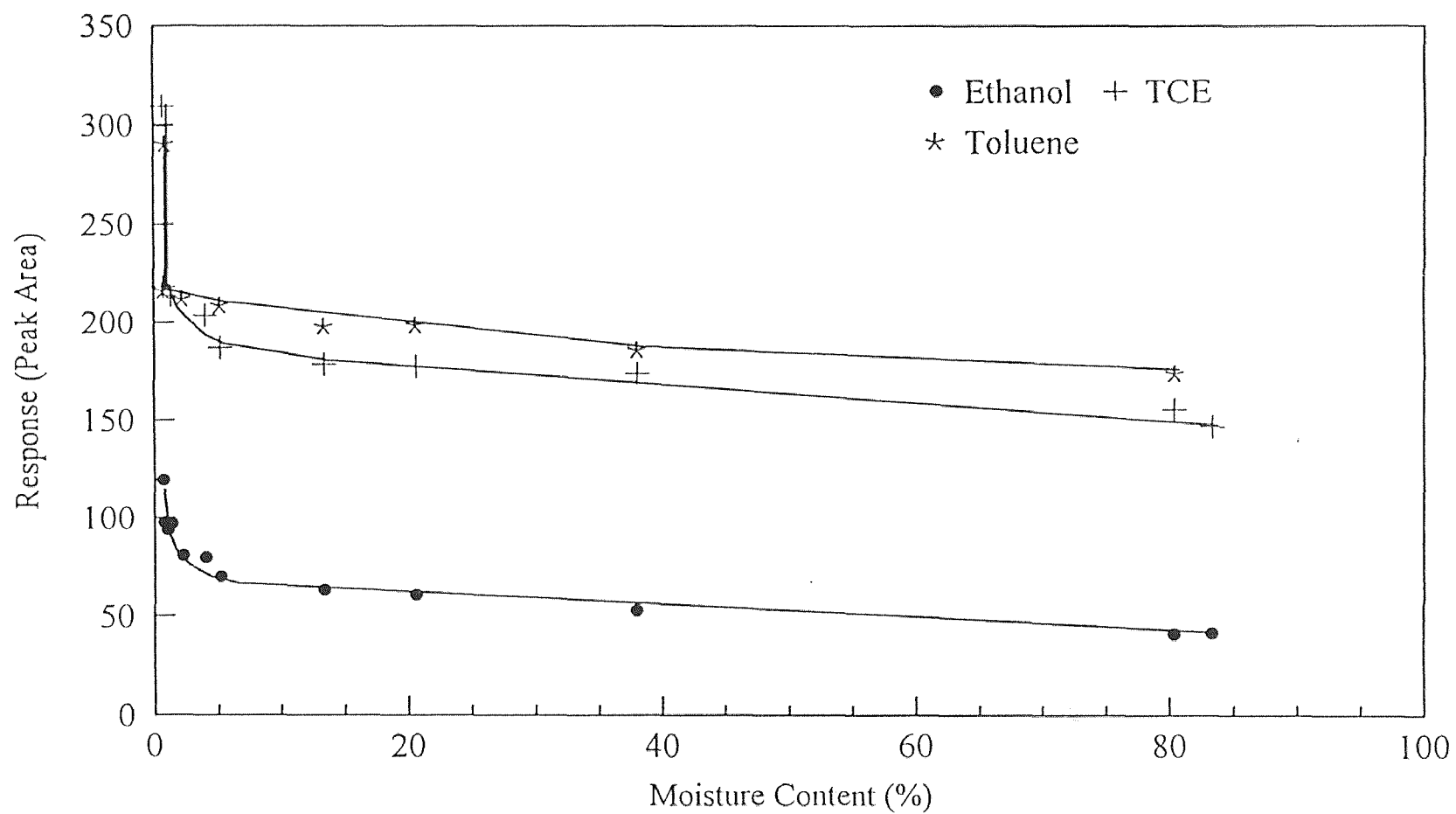


Figure 11 Effect of Moisture in Sample Air

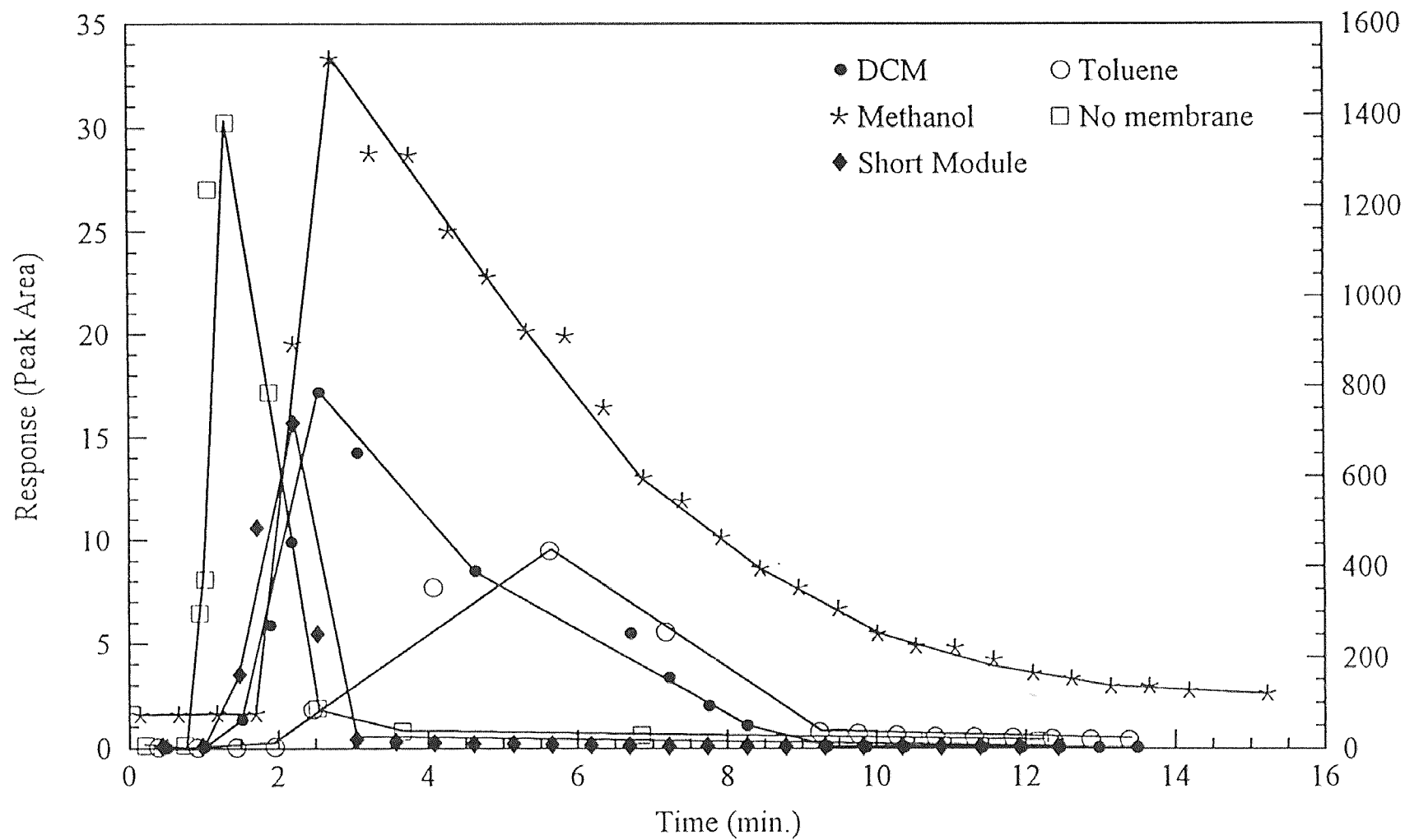


Figure 12 Response Time of the Analytic System

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